Velocity-modulated infrared laser spectroscopy of molecular ions: The \( \nu_1 \) band of HNN\(^+\)

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Protonated nitrogen (HNN\(^+\)) has been of central importance in establishing the predominance of ion–molecule reactions in interstellar cloud chemistry and has provided a convenient test case for the development of laboratory techniques for studying charged molecules in general.\(^1\) It is a member of the isoelectronic series of linear triatomic molecules containing hydrogen and two first row atoms (HCN, HNC, HCO\(^+\), HO\(^+\), HNN\(^+\)); this series has been an important prototype system for theoretical and experimental studies of isomerization, collisional dynamics, chemical reactivity, bonding, and molecular structure. Experimental spectroscopic information of HNN\(^+\) has been limited, however, to millimeter- and submillimeter wavelengths,\(^2\) and therefore vibrational frequencies and anharmonicities have not been measured. An extensive search in various glow discharges for pure rotational transitions within excited vibrational manifolds has proven unsuccessful;\(^5\) the successful detection of vibrational satellites of the isoelectronic molecular ion HCO\(^+\) under similar conditions suggests that chemical and dynamical processes are markedly different for these two species.\(^5\) Hence the need for vibrational spectroscopy of HNN\(^+\) is evident. In this paper we report the first detection and measurement of the 3.1 \( \mu \)m \( \nu_1 \) (NH stretch) vibration–rotation band of protonated nitrogen produced in an ac glow discharge using velocity-modulation and simple lock-in detection.

The experimental arrangement is shown schematically in Fig. 1 and is essentially the same as that reported previously in the detection of the \( \nu_1 \) band of HCO\(^+\).\(^6\) An amplitude stabilized Kr\(^+\) laser is used to pump a Burleigh color center laser system, producing 0.1–10.0 mw of narrow band (1 MHz) cw radiation tunable from 3100 to 4500 cm\(^{-1}\) which is directed through a 0.009 \( \times \)1.0 m liquid nitrogen cooled discharge cell and detected with an InSb photovoltaic detector. A 1.3 kHz ac discharge, generated by a symmetric bipolar square wave supplying 350 W at 6 kV \( p-p \) to the hot electrode, and lock-in detection at the discharge frequency yield the first derivative line shapes shown in Fig. 2. Maximum signal strength was obtained in a 10/1 mixture of \( \text{H}_2 \) and \( \text{N}_2 \) at a total pressure of 800 mTorr and maximum available discharge current (70 mA).

A total of 43 transitions [\( R(19) - R(0) \), \( P(1) - P(23) \)] were observed and measured to an accuracy of \( \pm 100 \) MHz using a Burleigh wave meter. The transition frequencies have been fit to a fourth order polynomial of the form

\[
\tilde{\nu} = \nu_0 + (B \nu + B' \nu^2) m + (B'' \nu - B'' \nu^2 - D \nu + D \nu^2)m^2
- 2(D' \nu + D'' \nu^2)m^3 - (D'' \nu - D'' \nu^2)m^4,
\]

from which the vibrational frequency (\( \nu_0 \)) and the rotational constants (\( B_0 \) and \( D_0 \)) have been calculated (Table...
TABLE I. Measured spectroscopic constants (cm\(^{-1}\)) for HNN\(^+\).

| This work | Hennig, Kraemer, and Diercksen\(^1\); the extremely good agreement of the rotational constants indicates that the relative precision of the wave meter is nearly an order of magnitude better than its quoted absolute accuracy, and that highly accurate rotational constants can be determined rather simply. The analysis also yields excited state rotational constants; the small negative value of \(\Delta B' - \Delta B''\) indicates that the \(\nu_1\) vibrational level is essentially unperturbed by accidental Fermi and Coriolis resonances. Addition of sextic rotational constants \((\eta)\) to the fit resulted in negligible changes in the parameter values quoted in Table I and did not reduce the residuals.

Several comments regarding the behavior of HNN\(^+\) observed with the velocity-modulation technique and a comparison of these observations with those for HCO\(^-\) can be made. Both HNN\(^+\) and HCO\(^-\) absorption signals were optimized in 10/1 mixtures of H\(_2\) and N\(_2\) or CO at \(\sim 800\) mTorr and at maximum discharge currents. Furthermore, both ions were observable only in liquid nitrogen cooled discharge cells and both exhibited a rotational distribution consistent with \(T_{\text{rot}} \approx 300\) K. The HNN\(^+\) signals were, however, a factor of 2 stronger than those of HCO\(^-\). Because the intensity of these signals depends upon both the density and the drift velocity of the absorbing species, only qualitative conclusions regarding these parameters can be drawn; assuming the mobility and electric field strength to be similar in both systems, the more intense HNN\(^+\) spectrum indicates a higher density compared to that of HCO\(^-\). Whether this results from a 50/50 branching ratio of HCO\(^-\)/HOC\(^+\) formation in conjunction with slow isomerization, rapid chemical pathways of HCO\(^-\) destruction, or a relatively high level of vibrational excitation in HCO\(^-\) presents an interesting problem of ion kinetics in a glow discharge environment. Quantitative measurements of drift velocity, vibrational excitation, and discharge composition will help to elucidate this situation.

This new technique permits the study of chemically complex molecular ions, and will augment the ion beam resonance techniques\(^3\) and direct absorption spectroscopy in clean dc discharges\(^8\) currently employed for infrared spectroscopy of charged molecules.

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**References**

1. IBM Postdoctoral fellow.